Supporting Information

Synthesis and characterization of an iron complex bearing a hemilabile NNNpincer for catalytic hydrosilylation of organic carbonyl compounds

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Materials; Physical Methods

All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Labmaster glovebox. Glassware was dried at 150 °C overnight. Diethyl ether, *n*-pentane, tetrahydrofuran, and toluene, were purified using a Pure Process Technology solvent purification system. Deuterated benzene was first dried with CaH₂, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. All reagents were purchased from commercial vendors and used as received. 1,8-Dibromo-3,6-di-*tert*-butyl-9*H*-carbazole, 1-bromo,3,6-di-*tert*-butyl-9*H*-carbazole, 3-*tert*-butylpyrazole, and Fe[N(SiMe₃)₂]₂ were prepared according to literature procedures. ¹⁻⁴ ¹H NMR data were recorded on Varian Inova 500 MHz spectrometer at 22 °C. Resonances in the ¹H NMR spectra are referenced either to residual CHCl₃ at $\delta = 7.26$ ppm, C₆D₅H at $\delta = 7.16$ ppm, and C₄H₇DO at $\delta = 3.58$. Solution magnetic susceptibilities were determined by the Evans method.⁵ Elemental analysis was conducted by Midwest Microlab, LLC (Indianapolis, IN).

Synthesis of HCztBu(PztBu)2

The synthetic method was adapted from literature procedures with slight modification.⁶ 1.28 g (2.93 mmol) of 1,8-dibromo-3,6-di-*tert*-butyl-9*H*-carbazole, 3.62 g (29.2 mmol) of 3-*tert*-butylpyrazole, 1.80 mL (1.40 g, 12.0 mmol) of N,N,N',N'-tetramethylethylenediamine, 3.30 g (29.4 mmol) of potassium *tert*-butoxide and 15 mL of DMF were combined in a round bottomed flask. The resulting slurry was degassed by three freeze-pump-thaw cycles. 2.08 g (14.5 mmol) of copper(I) oxide was added, and the reaction mixture was heated to 150 °C for 4.5 days under N₂. After cooling, 50 mL of diethyl ether was added, and the diluted solution was washed with 4×50 mL of 1 M hydrochloric acid, followed by 3×50 mL of 1 M ammonium hydroxide. 6 × 50 mL of 3 M ammonium hydroxide. The organic layer was dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure to give an off-white solid, which was recrystallized from a concentrated *n*-hexane solution (1.51 g, 98%). ¹H NMR (500 MHz, CDCl₃, δ): δ 10.30 (br, 1H, NH), 8.03 (d, 2H, *J* = 3.0, Ar*H*), 7.99 (d, 2H, *J* = 4.0, Ar*H*), 7.57 (d, 2H, *J* = 2.5, Ar*H*), 6.40 (d, 2H, *J* = 4.0, Ar*H*), 1.50 (s, 9H, C(CH₃)₃). 1.42 (s, 9H, C(CH₃)₃). Anal. Calcd for C₃₄H₄₅N₅: C 77.97, H 8.66, N 13.37. Found: C 78.04, H 8.59, N 13.39.

Synthesis of HCztBuPztBu

1.05 g (2.93 mmol) of 1-bromo,3,6-di-*tert*-butyl-9*H*-carbazole, 1.09 g (8.79 mmol) of 3-*tert*-butylpyrazole, 0.66 mL (0.51 g, 4.40 mmol) of N,N,N',N'-tetramethylethylenediamine, 0.99g (8.79 mmol) of potassium *tert*-butoxide and 15 mL of DMF were combined in a round bottomed flask. The resulting slurry was degassed by three freeze-pump-thaw cycles. 0.63 g (4.40 mmol) of copper(I) oxide was added, and the reaction mixture was heated to 150 °C for 3 days under N₂. After cooling, 50 mL of diethyl ether was added, and the diluted solution was washed with 4×50 mL of 1 M hydrochloric acid, followed by 3×50 mL of 1 M ammonium hydroxide, 6×50 mL of 3 M ammonium hydroxide. The organic layer was dried over anhydrous MgSO₄, filtered, and evaporated under reduced pressure to give an off-white solid, which was recrystallized from a concentrated *n*-hexane solution (1.04 g, 88%). ¹H NMR (300 MHz, CDCl₃, δ): δ 10.03 (br, 1H, NH), 8.10 (d, 1H, J = 1.6, ArH), 8.05 (d, 1H, J = 2.5, ArH), 7.98 (d, 1H, J = 1.8, ArH), 7.52 (dd, 1H, J = 8.5, 1.8, ArH), 7.49 (d, 1H, J = 1.4, ArH), 7.42 (dd, J = 8.4, 0.3, 1H, ArH), 6.40 (d, 1H, J = 2.5, ArH), 1.49 (s, 9H, C(CH₃)₃), 1.47 (s, 9H, C(CH₃)₃), 1.46 (s, 9H, C(CH₃)₃). Anal. Calcd for C₂₇H₃₅N₃: C 80.75, H 8.78, N 10.46. Found: C 81.02, H 8.75 N 10.34

Synthesis of (Cz^{tBu}(Pz^{tBu})₂)Fe[N(SiMe₃)₂], 1

To 97 mg (0.19 mmol) of HCz^{tBu}(Pz^{tBu})₂ suspended in diethyl ether (10 mL) at ambient temperature under N₂ atmosphere was added 76.8 mg (0.20 mmol) of Fe[N(SiMe₃)₂]₂. The resulting slurry was stirred overnight at ambient temperature. Volatiles were removed under reduced pressure to afford a golden yellow solid (112 mg, 82%). Crystals suitable for X-ray diffraction were grown from a concentrated *n*-pentane solution of the complex at -35 °C. ¹H NMR (500 MHz, C₆D₆, δ): 56.3, 28.5, 3.54, 1.25, 0.87, -2.46, -13.4. μ_{eff} (C₆D₆) = 5.1(3) μ_{B} . Anal. Calcd for C₄₀H₆₂FeN₆Si₂: C 65.01, H 8.46, N 11.37. Found: C 64.76, H 8.25, N 11.20.

Synthesis of [(Cz^{tBu}(Pz^{tBu})₂)Fe]₂, 3

Method 1. To 101 mg (0.19 mmol) of HCz^{tBu}(Pz^{tBu})₂ in toluene (10 mL) at ambient temperature under N₂ atmosphere was added 109 mg (0.20 mmol) of Fe[N(SiMe₃)₂]₃. The solution was stirred overnight at 110 °C. Volatiles were removed under reduced pressure to afford a dark brown solid. Crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a THF solution at ambient temperature (44 mg, 20%). *Method 2*. To 53.5 mg (0.10 mmol) of HCz^{tBu}(Pz^{tBu})₂ in toluene (10 mL) at ambient temperature under N₂ atmosphere was added 50 mg (0.13 mmol) of Fe[N(SiMe₃)₂]₂. The solution was stirred overnight at 115 °C. Volatiles were removed under reduced pressure to afford a dark brown solid. Crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a THF solution at ambient temperature under N₂ atmosphere was added 50 mg (0.13 mmol) of Fe[N(SiMe₃)₂]₂. The solution was stirred overnight at 115 °C. Volatiles were removed under reduced pressure to afford a dark brown solid. Crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a THF solution at ambient temperature (44 mg, 18%). ¹H NMR (500 MHz, C₆D₆, δ): 56.3, 28.5, 3.54, 1.25, 0.87, -2.46, -13.4. Anal. Calcd for C₆₈H₈₆Fe₂N₁₀: C 70.70, H 7.50, N 12.13. Found: C 70.54, H 7.64, N 12.04.

1 catalyzed hydrosilylation

A mixed solution of the organic carbonyl compounds (1 or 3 equiv, 0.08 or 0.24 mmol), PhSiH₃ (0.08 mmol), and hexamethylbenzene as an internal standard in 0.5 mL of C_6D_6 was added to 1 (1 mol% based on PhSiH₃) in a J-Young NMR tube. The conversions and turnover numbers were calculated by ¹H NMR measurement based on the amount of the internal standard.

X-ray Crystallographic Analysis

Data were collected using either a Bruker Kappa ApexII (1) or a Bruker Quest CMOS diffractometer (2 and 3). Both instruments feature I μ S Mo-K $_{\alpha}$ radiation ($\lambda = 0.71073$ Å) microsources with laterally graded multilayer (Goebel) mirrors for monochromatization (Quazar and Helios Optics, respectively). Single crystals were mounted on Mitegen loop or micromesh mounts using a trace of mineral oil and cooled insitu to 100 K. Frames for all compounds were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX2.⁷ For all structures, the intensity data were corrected for absorption using multi-scan techniques (SADABS or TWINABS).⁸

The structure of **1** was solved using Superflip⁹ using a charge flipping algorithm which provided most nonhydrogen atoms from the E-map and the space group was assigned based on the electron density map. The structure was refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.¹⁰ Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. The structure contains significant disorder, which was resolved successfully. The two-part disorder was modeled that the occupancies of the major and minor components summed to **1**. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms are generated geometrically, with $U_{iso}(H)$ set to a multiple of $U_{eq}(C)$ with 1.5 for all CH units.

For the structures of **2** and **3** the space groups were assigned based on intensity statistics and systematic absences using XPREP within the SHELXTL suite of programs^{11, 12} and the structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares against F^2 with all reflections using

Shelxl2014¹³ using the graphical interface Shelxle¹⁴. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms are generated geometrically, with $U_{iso}(H)$ set to a multiple of $U_{eq}(C)$ with 1.2 or 1.5 for all CH units.

For 2, the crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell Now, with the two components being related by a 180 degree rotation around the reciprocal a-axis. The two components were integrated using Saint and corrected for absorption using TWINABS, resulting in the following statistics:

20873 data (3398 unique) involve domain 1 only, mean I/sigma 24.7 20234 data (3357 unique) involve domain 2 only, mean I/sigma 13.1 42073 data (7896 unique) involve 2 domains, mean I/sigma 19.7

The exact twin matrix identified by the integration program was found to be

1.00110 0.41458 0.43505 -0.00282 -1.00061 -0.00070 -0.00237 -0.00038 -1.00048

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.208(1).

The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2009)).

Crystal data and details of data collection 1–3 are given in Table S1 and S2.

Computational Details

All calculations were performed using density functional theory as implemented in the Orca computational software package.¹⁵ Geometry optimizations for all complexes were performed with the B3LYP functional, and def2-SVP¹⁶ basis sets. Reevaluation of the electronic energies (single point energy corrections) was done with def2-TZVP basis set. Additionally, the Fe center was treated with the DKH2 effective core potential to increase computational efficiency. Vibrational/rotational/translational entropies of the solute(s) were included using standard thermodynamic approximations. Solvation energies were determined by a self-consistent reaction field (SCRF) approach. Solvation calculations were carried out on optimized gas phase geometries employing the dielectric constant of $\varepsilon = 2.27$ (benzene). The standard set of optimized radii were used to generate the solute surface. All structures were verified to be minima on the potential energy surface by the removal of imaginary frequencies. Determination of the change in solution phase free energy $\Delta G_{(sol)}$ was calculated as follows:

$$\Delta G_{(\text{sol})} = \Delta G_{(\text{gas})} + \Delta \Delta G_{\text{solv}}$$
$$\Delta G_{(\text{gas})} = \Delta H_{(\text{gas})} - T\Delta S_{(\text{gas})}$$
$$\Delta H_{(\text{cas})} = \Delta E_{(\text{scf})} + \Delta ZPE$$

 $\Delta G_{(gas)}$ = change in gas phase free energy; $\Delta \Delta G_{solv}$ = change in free energy of solvation; $\Delta H_{(gas)}$ = change in gas phase enthalpy; T = temperature (298.15 K); $\Delta S_{(gas)}$ = change in gas phase entropy; $\Delta E_{(scf)}$ = self-consistent field energy or the electronic energy at the triple- ζ level; ΔZPE = change in vibrational zero point energy, and $\Delta G^{EA}_{(sol)}$ = electron attachment free energy in the gas phase.

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1		2		3 ^b	
Fe1–N1	2.091(2)	Fe1–N1	2.335(4)	Fe1–C1	2.105(3)
Fe1–N3	1.978(3)	Fe1–N3	1.961(3)	Fe1–N3	1.963(3)
Fe1–N6	1.906(3)	Fe1–N4	2.301(3)	Fe1–N5	2.120(3)
Fe1H73	2.502	Fe1–O1	1.826(3)	Fe1-C1#1	2.171(3)
Fe1H281	3.057	Fe1–O2	1.849(3)	Fe1…Fe1#1	2.698
N1–Fe1–N3	89.1(1)	N1-Fe1-N3	89.6(1)	C1–Fe1–N3	88.9(1)
N3–Fe1–N6	137.9(1)	N3–Fe1–N4	88.8(1)	N3–Fe1–N5	85.9(1)
N1-Fe1-N6	124.9(1)	O1-Fe1-O2	135.7(1)	N5-Fe1-C1#1	110.9(1)
				C1-Fe1-C1#1	101.8(1)
				Fe1-C1-Fe1#1	78.2(1)
		C8-C9-N2-N1	41.5(5)		
		C19-C18-N5-N4	35.1(5)		

Table S1. Selected bond distances (Å) and angles (°) for $1-3.^{a}$

^{*a*} Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in **Fig. 1–3**. ^{*b*} Symmetry operation: #1, -x, -y, -z.

ble S2. Crystal data and structure refinement details for 1–3.

	1	2	3
Empirical formula	$C_{40}H_{62}N_6Si_2Fe$	$C_{40}H_{62}N_5O_2Si_2Fe$	$C_{68}H_{86}N_{10}Fe_2$
Formula weight	813.21	756.97	1155.17
Space group	$P\overline{1}$	$P 2_1/n$	$P\overline{1}$
a/Å	13.6609(3)	9.3471(11)	10.6257(7)
<i>b</i> /Å	16.2506(5)	18.745(3)	11.7461(7)
c/Å	22.6277(6)	24.074(3)	13.3730(9)
$a/^{\circ}$	85.8334(18)	90	108.574(3)
$b/^{\circ}$	77.5244(16)	91.099(6)	101.586(4)
$g/^{\circ}$	72.8578(15)	90	98.224(4)
$V/Å^3$	4686.59(12)	4217.3(9)	1510.91(17)
Ζ	4	4	1
D_{calcd} , g cm ⁻³	1.152	1.192	1.270
F(000)	1760.0	1628.0	616.0
Temp, K	100	100	100
<i>R</i> (F), %	8.31	9.00	5.66
$R_{\rm w}({\rm F}),\%$	26.2	17.43	13.83



Fig S1. Optimized structure of 1 (S = 2) and optimized structure of proposed three- and four-coordinate intermediate. Grey, blue, lilac, and yellow spheres represent C, N, Fe, and Si atoms, respectively.



Fig S2. ¹H NMR spectrum of 1. * solvent residual peaks.



Fig S3. ¹H NMR spectrum of 3. * solvent residual peaks.